

EFFECTIVE DATE

May 6, 1997

LANL-EES-4-DP-806, R2

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CHROMATOGRAPHIC DETERMINATION OF CONSTITUENT CONCENTRATIONS IN SOLUTION

LOS ALAMOS QUALITY PROGRAM



APPROVAL FOR RELEASE

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Yucca Mountain Site

Characterization Project

HISTORY OF REVISION

REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE
R0	01/31/96	N/A	This procedure supersedes LANL-EES-15-DP-326.
R1	06/13/96	3, 5-10	To better clarify the process.
R2	05/06/97	1, 7	Revised to comply with LANL-YMP-QP-06.3 requirements.

Los Alamos

Yucca Mountain Site

Characterization Project

CHROMATOGRAPHIC DETERMINATION OF CONSTITUENT CONCENTRATIONS IN SOLUTIONS

1.0 PURPOSE

This detailed technical procedure (DP) describes the methods used to determine the concentration of selected constituents in solution using ion-chromatography (IC) and high pressure liquid chromatograph (HPLC) technology. These determinations are made in support of the Reactive Tracer and Water Chemistry Studies for the Yucca Mountain Site Characterization Project (YMP).

2.0 SCOPE

This procedure applies to the calibration and use of systems for detection and quantification of constituents of interest in solution. These systems are used in the Los Alamos National Laboratory (LANL) YMP by LANL and LANL subcontractor personnel.

3.0 REFERENCES

LANL-YMP-QP-02.7, Personnel Training
LANL-YMP-QP-03.5, Documenting Scientific Investigations
LANL-YMP-QP-08.1, Identification and Control of Samples
LANL-YMP-QP-17.6, Records Management
LANL-EES-4-DP-802, Preparation of Standards for Tracer Concentration Measurements
Dionex Ion Chromatograph Manuals
Dionex Autoion 450 Data System Manuals
Column and ASRS Booklets
Water Absorbance Detector Manuals

4.0 DEFINITIONS

NA

5.0 RESPONSIBILITIES

- The Principal Investigator (PI)
- Users of this Procedure

6.0 PROCEDURE

The use of this procedure must be controlled as follows:

- If this procedure cannot be implemented as written, YMP personnel should notify appropriate supervision. If it is determined that a portion of the work cannot be

accomplished as described in this DP, or would result in an undesirable situation, that portion of the work will be stopped and not resumed until this procedure is modified, replaced by a new document, or current work practice is documented in accordance with QP-03.5, subsection 6.1.6.

- Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct revision of this procedure is used.

When this procedure becomes obsolete or superseded, it must be destroyed or marked “superseded” to ensure that this document is not used to perform work.

6.1 Principle

Typical materials for analysis are well water and solutions that are prepared for study of tracer interactions with geologic materials. The analysis method depends on such factors as the nature of the solution to be analyzed, concentration range of the target constituent, and expected interferences. The PI or DP user specifies the method for measuring the target constituent concentration, which may include descriptions of instrument configuration, column setup, run parameters, and sample and reagent preparation.

6.2 Equipment and Hardware/Software

The configuration generally consists of an Eluant Degas Module, Gradient Pump Module, Detector Module, Chromatograph Column Module, and Data Acquisition Module (with appropriate software). An example is the DIONEX System 4500i. An autosampler (and associated software) is an optional item that provides automatic analyses of samples on a predetermined schedule.

6.2.1 Equipment Malfunctions

Most malfunctions of the instrument module will prevent the module from operating, thereby generating no data or stopping operations. Examination of the instrument output relative to expected results will also indicate a malfunction. The analysis must be repeated after correction of the malfunction.

6.2.2 Safety Considerations

Safety concerns associated with operating the ion chromatograph are limited to securing and handling high-pressure supply gas cylinders. Safety considerations associated with handling of chemicals will depend on the chemical nature of the solutions being analyzed. Material safety data sheets (MSDSs) should be consulted to determine whether special protective clothing and/or eye protection are required. Hazardous chemical wastes should be disposed of properly.

6.2.3 Special Handling

Handling of all equipment associated with this DP should be done in accordance with manufacturer's or vendor's guidelines. Special handling of equipment or hardware should be considered on a case-by-case basis as the need arises. Any special handling should be documented in a laboratory notebook.

6.3 Preparatory Verification

After configuring the physical components of the system, the operator energizes the system components, loads the data acquisition software, and pressurizes the solution delivery and pressure valve systems. The operator ensures that the pressurized gas and solution delivery systems are not leaking and are safely operating, that each module is functioning electronically, and that the data acquisition program is responsive. The operator conducts checks recommended by the manufacturer, if applicable. Documentation of these checks is not necessary unless malfunctions are detected that may influence the quality of previously generated data. If this should occur, an evaluation of the impact of the malfunction on previously generated data is documented in a laboratory notebook. Operations do not continue until the malfunction is corrected.

6.3.1 Hold Points

NA

6.3.2 Calibration

Control of the equipment will be according to the instrument operating manual (e.g., Dionex Operations Manual).

6.3.2.1 Initially, a series of standard solutions of concentrations spanning the expected concentration range of the analytes is run (including replicates). The data is used for generation of a reference curve and to estimate the analytical uncertainty (subsection 6.5.3). If possible, preparation of standards associated with tracer experiments should be done in accordance with DP-802. Alternatively, standard preparation can be documented in a notebook in accordance with QP-03.5.

6.3.2.2 When a batch of samples is analyzed, the instrument is calibrated as follows:

- a. A series of standards that bracket the expected concentration range of the samples is run and a working linear or quadratic calibration curve obtained by measuring peak area or height against analyte concentration.

Software available with the chromatography instrumentation calculates the formula for the curve and the coefficient of determination (R^2). In order for the calibration curve to be acceptable the R^2 must be greater than or equal to 0.990. If the data does not meet this criteria, the standards should be rerun. If possible, preparation of standards associated with tracer experiments should be done in accordance with DP-802. Alternatively, standard preparation can be documented in a notebook in accordance with QP-03.5.

- b. The standardization is documented with the results as described in subsection 6.5.2.
- c. The same standards are run at regular intervals during the analysis of a series of samples. If these standards remain within 3 x the standard deviation as determined by the calibration curve then the sample concentrations are considered valid.
- d. Sample runs may be aborted if the operator suspects changes in instrument or analysis conditions that could invalidate the results.

6.3.3 Environmental Conditions

The operator ensures that the instrument, samples, and reagents are conditioned to the same room temperature, an exact and controlled instrument or sample temperature is not critical to quality analysis. An instrument warm-up period and solution conditioning period of one hour is generally sufficient. Checks on temperature do not need to be documented. Work should be conducted under normal laboratory conditions of cleanliness.

6.4 Control of Samples

Samples prepared for analysis are controlled according to QP-08.1. All samples should be stored in such a way that evaporation of water is minimized or eliminated during storage (e. g., by storing them in tightly capped bottles, sample refrigeration is not required for samples stored up to one year). The sample container material should be chosen to avoid contamination and the potential sorption of constituents to the containers walls. Any special procedures followed to desorb constituents prior to analyses should be documented in a laboratory notebook. If there is any question about sorption to container walls, batch sorption experiments should be conducted (and documented in a laboratory notebook) using the constituents and labware in question. Special storage and handling requirements for different constituents should be considered on an individual basis, and the storage and handling of all samples to be analyzed should be documented in a laboratory notebook so that a sample

handling history is maintained. This documentation should be done in accordance with QP-08.1.

6.5 Implementing Procedure

6.5.1 Sample Analysis

6.5.1.1 Sample solutions to be analyzed are prepared according to experimental procedures defined and specified by the PI or DP user, and documented according to subsection 6.5.2.

6.5.1.2 Prepare the sample for analysis as follows:

- a. If suspended solids are present, filter the sample or allow solids to settle and decant.
- b. Dilute the sample if necessary to bring the analyte concentration into the range established by the calibration.
- c. If using an autosampler, load the samples into the sampler vials. Enter the sample IDs in the program's scheduler, including any dilution factors. Calibration standards should be identified as part of the schedule.

6.5.2 Documentation of Results

6.5.2.1 To accommodate wide concentration ranges, variations in matrices, analytes selected for analysis, and specific interferences, each analysis is conducted according to an operating procedure (OP) or method that contains instructions on specific instrument setup and run parameters. The OP or method is documented in a laboratory notebook and/or in the result report for the analyses (see subsection 6.5.2.2).

6.5.2.2 A result report is generated for each set of analyses. This report includes the sample identities, descriptions, constituent concentrations, and concentrations of any standard reference solutions that were run. This information is recorded in a spreadsheet computer file (Lotus, Excel), which is printed when the report is complete. The raw data files (generated by the computer that is interfaced to the chromatograph) are printed and included as attachments to a laboratory notebook.

6.5.2.3 Listings of operations or methods files used to describe the control, setup, and operation of the instrument are retained with the result report.

6.5.2.4 All critical analysis information, including the analytical procedure, are included in the result report and referenced in a laboratory notebook.

Information relative to standards preparation, sample preparation, and any pertinent observations (e.g., those required by supporting DPs) needed for proper interpretation of the results are recorded in the laboratory notebook. This information is cross-referenced to the result report.

6.6 Data Acquisition and Reduction

6.6.1 Calculations

The instrument response (chromatography peak height or area) for a sample is transformed into a concentration using the standard curve derived in subsection 6.3.2.2. Optimally, only the linear portion of the standard curve should be used to derive constituent concentration in the sample; however, a nonlinear portion of the curve can be used at the discretion of the PI or operator. Analytical uncertainty is calculated according to subsection 6.6.2.

6.6.2 Analytical Uncertainty

The uncertainty associated with a specific analysis will be determined from the reference curve (subsection 6.3.2.1). The reference curve is constructed by either running a series of standard solutions of concentrations spanning the range specified in the operating procedure (OP) or a range that includes the expected concentrations of the series of samples to be run. The results are fitted by least-squares, which generates a best-fit equation for the data. The uncertainty of a specific analysis is then derived from the difference between the $3 \times \text{SD}$ curve and the fitted reference curve at the measured response for the unknown and is presented as a percentage of the reading. Commercial linear and nonlinear least square-fitting software is used to derive the best-fit equations mentioned above.

6.6.3 Data Acceptance or Rejection Criteria

Acceptance limits cannot be established in this DP because several major variables (e.g., choice of specific procedure and differences in matrices) influence the accuracy and precision of the analysis. However, the PI reviews the data and associated records and determines the acceptability of the generated data. The PI may reject calibrations or measurements for any of the following reasons:

- anomalous results,
- instrument malfunction during the course of the calibration or measurement,

- operational deviations which call into question the accuracy of the results, and
- inadequate record keeping.

The identity of the rejected results and the basis for the rejection are recorded in the laboratory notebook and/or in the result report for the analyses.

6.7 Potential Sources of Error and Uncertainty

Potential sources of analytical uncertainty are discussed in subsection 6.6.2. The following additional sources of error and uncertainty may exist:

- temperature differences between samples,
- poor preparation of standards used for calibration, and
- presence of interfering ions in the unknowns that are not present in the calibration standards.

These sources of error and uncertainty can be minimized by exercising good laboratory technique and by carefully examining the analytical results.

7.0 RECORDS

Records generated as a result of this DP include the result report (subsection 6.5.2.2) and all applicable entries in laboratory notebooks or attachments to laboratory notebooks. The documentation should consist of any applicable items identified in Section 6.0. Laboratory notebooks should be kept in accordance with QP-03.5. All records should be submitted to the Records Processing Center in accordance with QP-17.6.

8.0 ACCEPTANCE CRITERIA

Proper completion and filing of the records listed in Section 7.0 constitute the acceptance criteria for this procedure.

9.0 TRAINING REQUIREMENTS

“Read-Only” training is required for this DP. Training is documented in accordance with QP-02.7.

10.0 ATTACHMENTS

NA